Oxidative potential and chemical composition of $PM_{2.5}$ in office buildings across Europe – The OFFICAIR study

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Abstract

In the OFFICAIR project, indoor and outdoor $PM_{2.5}$ samples were collected in office buildings across Europe in two sampling campaigns (summer and winter). The ability of the particles to deplete physiologically relevant antioxidants (ascorbic acid (AA), reduced glutathione (GSH)) in a synthetic respiratory tract lining fluid, i.e., oxidative potential (OP), was assessed. Furthermore, the link between particulate OP and the concentration of the PM constituents was investigated.

The mean indoor $PM_{2.5}$ mass concentration values were substantially lower than the related outdoor values with a mean indoor/outdoor $PM_{2.5}$ mass concentration ratio of 0.62 and 0.61 for the summer and winter campaigns respectively. The OP of $PM_{2.5}$ varied markedly across Europe with the highest outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} (% antioxidant depletion/m^3 air) values obtained for Hungary, while $PM_{2.5}$ collected in Finland exhibited the lowest values. Seasonal variation could be observed for both indoor and outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} with higher mean values during winter. The indoor/outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} ratios were less than one with 4 and 17 exceptions out of the 40 cases respectively. These results indicate that indoor air is generally less oxidatively challenging than outdoors. Correlation analysis revealed that trace elements play an important role in determining OP, in particular, the Cu content. Indoor air chemistry might affect OP since weaker correlations were obtained for indoor $PM_{2.5}$. Our findings also suggest that office workers may be exposed to health relevant PM constituents to a different extent within the same building.

Keywords: environmental health; indoor air quality; occupational exposure; office building; oxidative potential; $PM_{2.5}$

1. Introduction

Numerous epidemiological and toxicological studies have shown a relationship between ambient particulate matter (PM) exposure and adverse health effects in humans (Brook et al., 2010; Hoek et al., 2002; Laden et al., 2000; Schwartz et al., 2002). Different pathophysiological mechanisms have been proposed to explain PM`s contribution to respiratory and cardiovascular diseases; however, there are still remaining questions to be answered. Many of the air pollution related health outcomes are thought to derive from oxidative stress initiated by certain gaseous air pollutants (i.e., nitrogen dioxide, ozone) or PM constituents in the lung (Ayres et al., 2008; Kelly, 2003; Nel, 2005). The pulmonary epithelial cells are protected against undue oxidation by the respiratory tract lining fluid (RTLF) which contains low-molecular weight antioxidants (i.e., reduced glutathione, ascorbate, urate) and antioxidant enzymes. Either the increased exposure to oxidants or the presence of decreased antioxidant defenses could lead to oxidative stress which in turn can activate a number of redox sensitive signaling pathways (Anseth et al., 2005; Kelly, 2003; Kelly and Fussell, 2012). However, the identification of the oxidatively active components of PM is still a challenging task since particles vary in size, mass, number, shape, aggregation status, surface area as well as chemical composition.

Oxidative potential (OP) is a novel metric which is defined as a measure of the capacity of PM to oxidize target compounds. *In vitro* acellular methods based on different principles (i.e., antioxidant depletion, hydroxyl radical formation in the presence of H_2O_2, consumption of dithiotreitol, fluorescent probes) have been developed and used for the assessment of the OP of aerosol particles. Previous studies suggest that various chemical compounds such as certain transition metals (e.g., Fe, Cu, Cr), aromatic organic compounds (e.g., quinones) and some major PM constituents (e.g., humic-like substances) contribute to particulate OP (e.g., Godri et al., 2010; Roginsky et al., 1999; Szigeti et al., 2015; Verma et al., 2012). The importance of the water-soluble part of the trace elements has also been proposed since higher correlations may occur between them and the OP metrics compared to the total trace element concentrations (Szigeti et al., 2015). Although, several studies have linked increased $PM_{2.5}$ mass concentration to adverse health effects, the use of OP in epidemiology has also been suggested as a promising metric since it may better represent the health impact of the aerosol particles (Borm et al. 2007;

Boogaard et al. 2012; Szigeti et al., 2015; Yang et al., 2015). However, there is still no consensus about which OP metrics are the most appropriate to predict PM-related health effects.

Outdoor locations (i.e., urban, rural, industrial sites) are well characterized (in terms of PM mass concentration and chemical composition) over almost the entire world due to the existing regulations on the mass concentration of PM_{10} and $PM_{2.5}$; however, less information is available about PM in indoor microenvironments, particularly in offices (Chatoutsidou et al., 2015; Sangiorgi et al., 2013; Saraga et al., 2011; Szigeti et al., 2014). Office buildings are generally located in big cities near traffic intersections and busy roads in order to make them easily accessible for the employees. These buildings are generally equipped with heating, ventilation and air conditioning (HVAC) system to improve the air quality and create an acceptable feeling of comfort for the office workers. The inlet of the HVAC system is generally located on the roof of the buildings where the air is thought to be less polluted due to the distance from the traffic-related sources compared to the ground level. The filtering effect of the mechanical ventilation system, indoor sources and sinks of aerosol particles as well as the different microclimatic conditions (i.e., temperature, relative humidity) all have an influence on the size and chemical composition of the indoor particles as well as on the indoor/outdoor PM mass concentration ratio (Meng et al., 2007). However, it is still a challenge to determine the indoor generated part of the concentration of indoor $PM_{2.5}$ mass and the PM constituents. Substantial fraction of outdoor particulate matter pollution infiltrates indoors (Hänninen et al. 2004). Building occupants have some influence on the infiltration by operating windows and doors and many studies have shown that during the summer time infiltration levels are higher than in winter (Hänninen et al. 2011).

Many indoor activities (e.g., cooking, smoking, incense and candle burning) as well as re-suspension of settled dust may contribute to indoor $PM_{2.5}$ mass concentration in residential homes (Urso et al., 2015); however, fewer indoor sources are apparent for offices. Particle emission from printers, photocopiers and multi-task devices are well-known sources for ultra-fine particles, but these have almost no impact on the $PM_{2.5}$ mass concentration (e.g., Destaillats et al., 2008; He et al., 2007). Re-suspension of settled particles (with aerodynamic diameter larger than 1 μm) from indoor surfaces are common particle sources in offices (Chatoutsidou et al., 2015). Some specific activities (i.e., enveloping) could also contribute to the concentration of certain PM constituents (Szigeti et al., 2014). Furthermore, *in-situ* ozone-initiated chemistry with reactive volatile organic compounds could lead to the formation of secondary organic aerosol (Weschler

and Shields, 1999). However, it is likely that particles of outdoor origin are still the most important determinants of $PM_{2.5}$ in these environments compared to the indoor generated particles.

The spatial and temporal variation of particulate OP is not as well characterized as the mass concentration and chemical composition of PM. Moreover, only a very limited information is available about the OP of indoor PM. In the frame of the European Union project OFFICAIR (on the reduction of health effects from combined exposure to indoor air pollutants in modern offices), indoor and outdoor $PM_{2.5}$ samples were collected in office buildings to facilitate (i) the OP assessment and chemical characterization of the particles and (ii) the investigation of the relationship between particulate OP and PM constituents. Furthermore, the aim of this study was to fill some gaps and answer some questions regarding the indoor and outdoor environment.

2. Experimental

2.1. Description of sampling sites and instrumentation

The selection of the office buildings was made according to predefined criteria developed during the OFFICAIR project (Bluyssen et al., 2015). For highlighting regional similarities and differences in aerosol characteristics, sampling sites were selected in different regions across Europe. $PM_{2.5}$ samples were collected in Finland (FI), Greece (GR), Hungary (HU), Italy (IT) and The Netherlands (NL) in a total of 20 office buildings (n = 5 for GR and HU, n = 4 for IT and n = 3 for FI and NL). The location of the sampling sites is depicted in Fig. A.1. $PM_{2.5}$ was sampled at one indoor and one outdoor location per building for approximately 100 h (from Monday 9 AM until Friday 5 PM) during summer 2012. The sampling campaign was repeated in winter 2012/2013. In order to investigate spatial variability within an office building, parallel indoor sampling (n = 2) was performed in one Dutch building (NL3) in April and May 2013. The indoor and concomitant outdoor $PM_{2.5}$ samples were collected onto quartz fiber filters (Ø 47 mm and Ø 37 mm, Whatman QM-A) supplied by GE Healthcare (Little Chalfont, Buckinghamshire, UK). Field blank samples were also collected. Before sampling, filters were wrapped in aluminium foil and pre-treated at 550°C in an electric oven for 8 h in order to eliminate any possible organic contaminants. Thereafter filters were conditioned in an acclimatized room for 48

h at 20 ± 1°C and 50 ± 5% relative humidity, and then weighed on a Mettler Toledo XP26DR balance with a readability of 2 µg. Low-volume aerosol samplers equipped with a $PM_{2.5}$ head operating at a constant flow rate of 0.24 - 2.3 m^3 h^{-1} were used. The sampling head was placed at 1.2 m height (sitting height) in the indoor locations. Two sampling strategies were applied for the outdoor $PM_{2.5}$; at the air inlet of HVAC systems or at the same height as that which the indoor sampling took place since, in some cases, it was not possible to perform the outdoor sampling at the inlet of the HVAC system. In the case of Greece and Hungary, all buildings were selected in the corresponding capital cities: Athens and its metropolitan area and Budapest. Two of the Dutch monitored buildings were located in Delft, while one was in the resort settlement of Noordwijk. Two of the Italian buildings chosen were in Florence, one in the center of Milan and another one in the metropolitan area of Milan. Furthermore, office buildings located in a small (Varkaus) and in a medium sized city (Kuopio) were selected in Finland. The main characteristics of the monitored buildings are compiled in Table 1. The windows of the offices were generally kept closed throughout the study; however, episodes of opened windows were registered during the summer sampling campaign in some office buildings. During the sampling period, indoor and outdoor air temperature and relative humidity were monitored close to the PM samplers with a time resolution of 5 min.

place of Table 1

2.2. Chemical characterization of $PM_{2.5}$

Loaded as well as field blank filters were subjected to different chemical analyses in order to determine the concentration of trace elements, major water-soluble ions as well as organic and elemental carbon (OC and EC respectively) by the methods described in details elsewhere (Mihucz et al., 2015). Briefly, 1/3 of each filter was cut out with a ceramic lance and then subjected to vapor-phase microwave-assisted *aqua regia* extraction and the concentration of 16 trace elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Sn, Sb and Pb) was determined by inductively coupled sector field mass spectrometry (ICP-SF-MS; ELEMENT2; ThermoFinnigan, Germany). Another 1/3 of each filter underwent a sonication-assisted water extraction and the concentration of the major water-soluble ions and the water-soluble part of the trace elements were determined by ion chromatography (881 Compact IC pro system; Metrohm,

Switzerland) and ICP-SF-MS respectively. One cm^2 of each filter was punched out and used for the OC/EC analysis by means of an OC/EC analyzer (Sunset Laboratory, USA) and the default temperature program of the EUSAAR-2 protocol (Cavalli et al., 2010). The sampling artefact of OC was not investigated for the indoor and outdoor samples in this study. It should be noted that the comprehensive chemical characterization of the $PM_{2.5}$ samples collected in Finland and Hungary was failed due to the low amount of PM collected as a result of the low air flow rate ($0.24\ m^3\ h^{-1}$) used during sampling.

2.3 Assessment of particulate oxidative potential

An acellular method based on the determination of antioxidant consumption was applied for the assessment of the particulate OP. The extent to which these antioxidants are depleted by PM reflects a direct measure of their oxidative activity. For this purpose, a synthetic RTLF containing the antioxidants, urate, ascorbate and reduced glutathione in a physiologically relevant concentration of 200 µmol L^{-3} each was prepared and used (Godri et al., 2010b; Szigeti et al., 2014). Briefly, 5-mm discs (n=3) were punched from the loaded and field blank filters and incubated at 37 °C for 4 h in 0.5 mL of the model RTLF. After centrifugation, the concentration of urate and ascorbate was determined by reversed-phase high performance liquid chromatography with electrochemical detection (Gilson Scientific Ltd., UK) based on a modified method of Iriyima et al. (1984). Total glutathione and reduced glutathione were determined by enzyme-linked 5,5'-dithio-bis(2-nitrobenzoic acid) assay by using a microplate reader (SpectraMAX 190; Molecular Devices, UK) and based on the method of Baker et al. (1990). For quality assurance, particle-free and known particle controls were run in parallel with the $PM_{2.5}$ samples. The detailed calculation method of the OP metrics has been described elsewhere (Godri et al., 2010).

2.4. Statistical data evaluation

Pearson's linear (r) and Spearman's rank correlation coefficients (r_s) with a two-tailed test of significance (p) were produced to show relationships between different PM characteristics by using the software package of IBM SPSS Statistics for Windows, version 21 (IBM Corp.,

Armonk, NY, USA). Significant correlation was defined as $p < 0.05$. The Shapiro-Wilk test was used to determine the distribution of data and subsequently the type of the correlation analysis (parametric /Pearson's correlation/ or non-parametric /Spearman's rank correlation/).

3. Results

3.1. Temporal and spatial patterns

3.1.1. $PM_{2.5}$ mass concentration

Table 2 presents the seasonal variability of the indoor and outdoor $PM_{2.5}$ mass concentration as well as the indoor/outdoor $PM_{2.5}$ mass concentration ratio for each country. Considerable spatial and temporal differences in the outdoor $PM_{2.5}$ mass concentration values could be observed among the study areas and seasons. The lowest average values were obtained in Finland for both seasons, while the highest mean values were measured in Greece and in Hungary during summer and winter respectively. The highest seasonal variation for outdoor $PM_{2.5}$ mass concentration was observed in Hungary where also the highest contrast was recorded between the ambient temperature values during the summer (mean value: 26.3 °C) and the winter campaigns (mean value: 3.6 °C).

place of Table 2

A strong correlation ($r=0.74$; $p<0.01$) was observed between the indoor and outdoor mass concentration values. The indoor $PM_{2.5}$ mass concentration was always lower than the corresponding outdoor value, except for two cases when the outdoor $PM_{2.5}$ mass concentration was lower than 10 $\mu g\ m^{-3}$ in Finland and Italy. The indoor/outdoor $PM_{2.5}$ mass concentration ratio values obtained for the summer and the winter campaigns were compared (paired t-test) and no association was found between them. Less than 20% difference in the indoor $PM_{2.5}$ mass concentration values was obtained in the case of the Dutch building where parallel indoor sampling was carried out (Table A.1).

3.1.2. Oxidative potential

The OP of $PM_{2.5}$ also varied markedly across the investigated sites (Fig. 1). Similar to our previous observations, urate was not depleted by $PM_{2.5}$ (e.g., Szigeti et al., 2014). To aid interpretation, the OP metrics are depicted in OP^{AA} m^{-3} and OP^{GSH} m^{-3} (% depletion/m^3 air) as well as OP^{AA} μg^{-1} and OP^{GSH} μg^{-1} (% depletion/μg PM) units in Fig. 1. The former are considered as exposure metrics, while latter ones point out the ability of the particles to deplete physically relevant antioxidants.

place of Fig. 1

The maximum values for outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} were about 30 and 90 times higher than the lowest ones respectively. The lowest indoor and outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} values were obtained for $PM_{2.5}$ collected in Finland, while the outdoor samples collected in Hungary exhibited the highest activities during both seasons. In the case of indoor OP^{AA} m^{-3} and OP^{GSH} m^{-3}, $PM_{2.5}$ samples collected in Hungary during winter showed the highest values. Seasonal variation could be observed for both indoor and outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} with higher mean values during winter with some exceptions. On average, the mean indoor/outdoor OP^{AA} m^{-3} ratio was 0.64 (median: 0.60) and 0.78 (median: 0.71) for the summer and winter campaigns respectively. A considerably larger seasonal difference was observed for the mean indoor/outdoor OP^{GSH} m^{-3} ratio with values of 3.21 (median: 0.67) and 1.45 (median: 1.14) for summer and winter respectively. The large difference in the mean and median OP^{GSH} m^{-3} values is due to the outliers obtained in The Netherlands (e.g., maximum indoor/outdoor OP^{GSH} m^{-3} ratio of 25). The indoor/outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} ratio was larger than one in 4 and 17 cases out of the 40 respectively. Strong correlation was observed between the indoor and outdoor OP^{AA} m^{-3} (r_s=0.68; $p<0.01$); however, indoor and outdoor OP^{GSH} m^{-3} values were not correlated (r_s=0.13).

The spatial and temporal variability was moderate for OP^{AA} μg^{-1}; however, substantial differences were obtained for OP^{GSH} μg^{-1} (Fig. 1). The highest outdoor OP^{AA} μg^{-1} and OP^{GSH} μg^{-1} values were apparent for Hungary and Italy during summer, while the $PM_{2.5}$ samples collected in The Netherlands showed the highest depletion rate for glutathione regarding the indoor environment. The indoor/outdoor OP^{AA} μg^{-1} and OP^{GSH} μg^{-1} ratio was larger than one in 26 and 23 cases out of the 40 respectively. Indoor OP^{GSH} μg^{-1} values were significantly higher than the corresponding outdoor ones in the case of all samples collected in The Netherlands; however, considerably lower outdoor OP^{GSH} μg^{-1} levels were measured for the Dutch buildings compared to the other office buildings.

3.1.3. Concentration of PM constituents and chemical mass closure

The contribution of the investigated PM constituents to the $PM_{2.5}$ mass is depicted for the summer and winter campaigns in Fig. 2. For the purpose of chemical mass closure, the concentration of organic matter (OM = 1.6 × OC), sea salt (from standard seawater composition using Na^+ as tracer), non-sea-salt SO_4^{2-} ($[nss\text{-}SO_4^{2-}] = [SO_4^{2-}] - 0.231 \times [Na^+]$; the factor of 0.231 is the average mass concentration ratio of SO_4^{2-} to Na^+ in sea-water) and other ions (non-sea-salt fraction of $[Ca^{2+}] + [Mg^{2+}] + [K^+]$) were calculated. It should be noted that the approaches used for the calculation of OM and sea salt contain uncertainty since (i) the average organic molecular weight per carbon weight varies with location and season as the mix of organic compounds in $PM_{2.5}$ varies and (ii) it is assumed that the Na^+ is only formed from sea spray.

place of Fig. 2

On average, 82% of the gravimetric mass could be reconstructed by the chemical measurements. OM was the major component of the outdoor $PM_{2.5}$ collected in Greece and in Italy for both seasons, while NO_3^- represented the highest contribution in the case of $PM_{2.5}$ collected in The Netherlands. The relative contribution of OM to the mass of the indoor $PM_{2.5}$ was higher than in the case of the corresponding outdoor $PM_{2.5}$ by factor of 1.5, on average. However, the concentration of OM (expressed in $\mu g\ m^{-3}$) was still lower in the indoor $PM_{2.5}$ compared to the outdoor $PM_{2.5}$ in 82% of the cases due to the low indoor/outdoor mass concentration ratios. Besides spatial variation, seasonality could also be observed for OM concentration with higher values during winter for both indoor and outdoor $PM_{2.5}$ while the concentration of EC was relatively constant at all sites during summer and winter. However, higher EC concentration values were observed for the office buildings located in big cities (Athens, Milan) with significant road traffic than for those located in smaller cities (e.g., Noordwijk).

Among the major water-soluble ions, $nss\text{-}SO_4^{2-}$, NO_3^- and NH_4^+ were the dominant ions in both indoor and outdoor $PM_{2.5}$. A winter peak was observed for the concentration of NO_3^-; however, no seasonality was observed for the concentration of $nss\text{-}SO_4^{2-}$ in neither Italy nor The Netherlands in contrast to Greece where the mean summer/winter concentration ratio was 2.2 and 2.3 for the indoor and outdoor $PM_{2.5}$ respectively. The indoor/outdoor NO_3^- concentration ratio was considerably lower than the corresponding indoor/outdoor $PM_{2.5}$ mass concentration ratio

when the outdoor mean temperature value was lower than the indoor one suggesting the evaporation of NH_4NO_3 (the main form of NO_3^- in $PM_{2.5}$) in the indoor environment. $PM_{2.5}$ samples collected in Milan were characterized by lower sea salt content since the sampling sites were far from any coastal areas (>100 km) in contrast to Athens (<18 km) or Noordwijk (<1 km) where the sea salt accounted for up to 8 and 26% of the $PM_{2.5}$ mass respectively. The sum of the molar concentrations of the water-soluble cations multiplied with their corresponding charge was almost equal to the sum calculated for the water-soluble anions (Fig. A.2). The median value of the cations/anions ratios was 1.04 (0.80 – 1.39) and 1.07 (0.86 – 1.36) for the indoor and outdoor $PM_{2.5}$ respectively.

The concentration of trace elements in the $PM_{2.5}$ varied widely among the sampling locations. The minimum and maximum concentration values obtained for the offices were listed in a previous publication (Mihucz et al., 2015). The indoor/outdoor trace element concentration ratios expressed in ng m^{-3}/ng m^{-3} and μg g^{-1}/μg g^{-1} are depicted in Fig. A.3. The median values of the indoor/outdoor trace element concentration ratios (expressed in ng m^{-3}/ng m^{-3}) were lower than one; however, values higher than one were observed for Cr, Cu and Cd in more than 25% of the cases. Regarding the indoor/outdoor ratios expressed in μg g^{-1}/μg g^{-1}, values higher than one were observed for Cr, Cd, V, Rb, Sr, Pb, and Sn in more than 50% of the cases. The water-soluble proportion of the elements expressed as the ratio of the concentration value obtained after water extraction and the concentration value obtained after *aqua regia* extraction is shown in Fig. A.4. The mean water soluble proportion was less than 25% for Al, Fe, Sn and Pb while the most water-soluble elements were V and Zn. Considerable differences in the water-soluble proportions could not be observed between the corresponding indoor and outdoor values. Similar water-soluble proportion values were observed for the $PM_{2.5}$ collected in Greece and The Netherlands; however, slightly different values were apparent in the case of some trace elements such as Sn, Cr, Mn and Cd in Italy.

3.2. Correlation between oxidative potential and PM characteristics

Taking into account all $PM_{2.5}$ samples, significant correlation was observed between $PM_{2.5}$ mass concentration and OP^{AA} m^{-3} (r_s=0.71, $p<0.01$). $PM_{2.5}$ mass concentration also correlated with OP^{GSH} m^{-3}(r_s=0.35, $p<0.01$); however, the correlation was not as strong at in the case of OP^{AA} m^{-}

^{3}. In the case of OP^{AA} m^{-3}, the correlation coefficient changed considerably when the samples were grouped into indoor (r_s=0.82, p<0.01) and outdoor (r_s=0.43, p<0.05) subcategories. Smaller deviation was observed between the correlation coefficients for the indoor (r_s=0.21, p=0.23) and outdoor (r_s=0.41, p<0.05) OP^{GSH} m^{-3} and $PM_{2.5}$ mass concentration.

place of Table 3

Carbonaceous fractions and major water-soluble ions correlated poorly with the OP metrics (Table 3) with some exceptions (e.g., OC and OP^{GSH}). Among the investigated trace elements, only the concentration of Cu correlated with both OP^{AA} μg^{-1} and OP^{GSH} μg^{-1} in the case of both indoor and outdoor $PM_{2.5}$. We noted considerable differences between the correlation coefficients obtained for the indoor and outdoor $PM_{2.5}$. Significant positive correlations between the concentration of 8 trace elements (Cu, Ni, Sn, Cd, Fe, Cr, Co and Pb) and OP^{AA} μg^{-1} were apparent for the outdoor $PM_{2.5}$. In contrast, only 2 trace elements (Cu and Mo) were relevant in the case of indoor $PM_{2.5}$. A similar trend could be observed for the correlation coefficients obtained between the water-soluble part of the trace element and OP^{AA} μg^{-1}. Fewer trace elements showed significant correlation with OP^{GSH} μg^{-1} compared to OP^{AA} μg^{-1} for both the indoor and outdoor $PM_{2.5}$.

4. Discussion

4.1. Geographical location, outdoor PM sources, infiltration and indoor PM sources: Which are the major determinants of indoor $PM_{2.5}$ mass concentration?

The outdoor $PM_{2.5}$ mass concentration values obtained in our study are consistent with the results reported elsewhere for the same areas (e.g., Kassomenos et al., 2014; Marcazzan et al., 2011; Putaud et al., 2010; Sillanpää et al., 2006; Szigeti et al., 2015). It is well-known that urban $PM_{2.5}$ mass concentration values are generally higher in Central and Southern Europe than in Northern Europe and most of the cities have difficulties with keeping the $PM_{2.5}$ mass concentration below the annual $PM_{2.5}$ mass concentration limit value (25 μg m^{-3}; EC, 2008). In line with this statement, considerably lower $PM_{2.5}$ mass concentration values were apparent for the sites investigated in Finland and in The Netherlands compared to Greece, Hungary and Italy.

Generally, only the indoor/outdoor concentration ratio is used to get information regarding whether people are exposed to higher concentration indoors or outdoors. However, this simple parameter does not allow for separating the outdoor particles from those generated indoors. Another approach estimates the infiltration factor as well as the amount of the indoor generated particles by using a marker compound which has no indoor source such as SO_4^{2-} (e.g., Hanninen et al., 2004; Sangiorgi et al., 2013). Moreover, the enrichment of an element in the indoor PM can be evaluated by calculating the indoor enrichment factor (EF) which is the ratio of the crustal EF of a constituent for the indoor PM to the crustal EF of the same constituent for the corresponding outdoor PM (Salma et al., 2013; Szigeti et al., 2014). One of the drawbacks of these methods is that there is no parameter which would take into account the evaporation of the semi-volatile compounds (e.g., NH_4NO_3) due to the change of temperature when outdoor particles penetrate into the offices.

Since (i) a strong correlation was observed between the indoor and outdoor $PM_{2.5}$ mass concentration values; (ii) the indoor/outdoor $PM_{2.5}$ mass concentration ratio was generally lower than one and (iii) the indoor/outdoor concentration ratio was also lower than one for all PM constituents with some exceptions, it can be assumed that, in general, the indoor $PM_{2.5}$ was not affected by any substantial indoor sources and the outdoor $PM_{2.5}$ mass concentration was still the major factor. It is also clear that the physical position and the proper operation of the HVAC system (e.g., efficient filtration; optimal air exchange rate) is important to reduce the PM mass concentration (Morawska et al., 2009; Quang et al., 2013); however, the determination of the exact infiltration rate is still challenging; the selection of the indoor and outdoor sampling locations, the frequency of windows opening; the filtering efficiency of the bag filters for the different particle sizes as well as the size distribution of the PM constituents all having an influence besides the evaporation of the semi-volatile compounds, sink (e.g., deposition on indoor surfaces), re-suspension and generation of aerosol particles. For example, it has been shown that an upgrade on the HVAC system could increase the overall efficiency of the system in removing particles from 58 to 86% (Morawska et al., 2009). Furthermore, the higher indoor/outdoor concentration values observed for some trace elements (e.g., Cd, Cu, Cr) in some cases suggest that they might have indoor sources. For example, Cd and Cr are associated with tobacco smoke (Slezakova et al., 2009) and office workers might take these compounds adsorbed on their clothes, skin or hair into the offices (thirdhand smoke).

4.2. Indoor air vs. outdoor air: Where is it better to stay?

If we approach the question from the angle of the $PM_{2.5}$ mass concentration, it is better to stay indoors than outdoors irrespective of the season since the indoor/outdoor $PM_{2.5}$ mass concentration ratios were less than one for the office buildings with only two exceptions. However, recent epidemiological studies focus on the chemical composition of PM, on the identification of those PM constituents which may be responsible for health outcomes and on the toxicologically relevant features of PM rather than the $PM_{2.5}$ mass concentration. The comparison of the mean indoor/outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} ratios with the mean indoor/outdoor $PM_{2.5}$ mass concentration ratio revealed that the mean indoor/outdoor ratios for the OP metrics were larger than the mean indoor/outdoor $PM_{2.5}$ mass concentration ratio especially in the case of OP^{GSH} m^{-3}. Furthermore, the indoor/outdoor ratios for OP^{AA} m^{-3} and OP^{GSH} m^{-3} were larger than one in more cases than the indoor/outdoor $PM_{2.5}$ mass concentration ratio; however, the mean indoor/outdoor ratio for the OP^{AA} m^{-3} was still lower than one, and similarly, the mean indoor/outdoor ratio for OP^{GSH} m^{-3} was lower than one in more than 50% of the cases. These OP results also suggest that staying indoors is generally better than spending time outdoors. However, the indoor/outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} ratios only imply whether office workers are exposed to oxidatively more challenging air indoors than outdoors or not. The considerable spatial and temporal differences observed for the OP metrics suggest that the office building characterized by indoor/outdoor OP^{AA} m^{-3} and OP^{GSH} m^{-3} ratios lower than one might have more health relevance compared to those characterized by ratios higher than one when the absolute indoor OP values are compared.

If the title of this section was “Indoor particles vs. outdoor particles: Which particles are considered to be more relevant in terms of OP?” then the answer would be less favorable for the indoor environment since the indoor particles generally showed considerably larger oxidative activity (especially OP^{GSH} μg^{-1}) than the outdoor particles on a per unit mass basis in our study. This observation (i.e., indoor/outdoor OP^{GSH} μg^{-1} and OP^{AA} μg^{-1} ratios were generally higher than the corresponding indoor/outdoor OP^{GSH} m^{-3} and OP^{AA} m^{-3} ratios) might be caused by several issues such as (i) the evaporation of those PM constituents which are not relevant in terms of OP in the indoor environment or (ii) higher filtration efficiency for the above-mentioned compounds

or (iii) the formation of reactive oxygen species in the indoor environment. This approach for the assessment of the OP is not relevant in terms of occupational exposure; however, it compares the ability of the indoor and outdoor particles to deplete physically relevant antioxidants.

The intensive investigation of PM oxidative activity through antioxidant depletion assays dates back to the early 2000s; several studies have been carried out at outdoor sites with different source characteristics (e.g., Font et al., 2014; Godri et al., 2010, 2011; Janssen et al., 2014); however, little is known about the OP of indoor PM. In our previous study we investigated the OP of $PM_{2.5}$ collected in Hungarian office buildings during the 8-h day shift (Szigeti et al., 2014). Similar to this study, higher OP^{GSH} μg^{-1} results were obtained for the indoor $PM_{2.5}$ compared to the corresponding outdoor data in three office building out of the five. To the best of our knowledge, there is no other published study about OP of indoor PM. A more complex investigation of the air pollutants is needed to fully answer the original question since there are also other health relevant air pollutants (e.g., formaldehyde, NO_2, O_3) and other health effects associated to PM constituents.

4.3. Linkage between PM constituents and particulate oxidative activity: Which are the relevant PM constituents?

Our findings on the correlations between the OP of outdoor PM and the concentration of PM constituents are in good agreement with previous observations (e.g., Godri et al., 2010, 2011; Künzli et al., 2006; Nawrot et al., 2009; Szigeti et al., 2015; Yang et al., 2014). Previous studies have shown that OP^{AA} and OP^{GSH} are sensitive to slightly different panels of metals and PM sources; OP^{GSH} is sensitive to traffic-related trace elements and OP^{AA} is more sensitive to regional PM constituents (e.g., Kelly et al., 2011). The statistical analysis revealed some differences for OP^{AA} and OP^{GSH}; more aerosol constituents were linked to OP^{AA} than OP^{GSH} as well as considerable differences were observed in the case of indoor and outdoor $PM_{2.5}$. However, the source apportionment analysis failed due to the low number of samples collected at each site. Previous studies have found heterogeneous associations between particulate oxidative activity and the concentration of PM constituents across European sites (Künzli et al., 2006; Nawrot et al., 2009) which may explain the low correlation coefficients observed for some PM constituents since all results for $PM_{2.5}$ collected in Greece, Italy and The Netherlands were

included in the correlation analysis. The heterogeneity may derive from the differences in the oxidation state, the chemical form as well as the bioavailable part of the same trace element at different sites since the sampling locations were characterized by different PM sources and meteorological conditions. The differences observed among the sites for the water-soluble proportions of the trace elements (Fig. A.4) also strengthen this assumption. In the case of the indoor $PM_{2.5}$, the weaker correlations suggest that the link between particulate OP and PM constituents is a more complex issue compared to the outdoor $PM_{2.5}$ and that the indoor air chemistry might play a crucial role in the formation of reactive oxygen species and other compounds which alter the oxidative properties of PM.

The pathways of particle-induced toxicity through antioxidant loss at the air–lung interface have already been discussed (Kelly and Fussell, 2012) and the trace elements (e.g., Cu, Sn, Ni, Fe) which showed strong and moderate correlations with the OP metrics in our study are in line with the proposed mechanism. The role of the water-soluble part of the trace elements does not appear to be significant since similar correlation coefficients were obtained between them and the OP metrics compared to the corresponding values obtained for the total trace element concentrations. However, firm conclusions cannot be made since the heterogeneity observed across the sites may have an effect as well. OC has not previously been identified as an indicator of OP^{GSH}; however, earlier studies found associations between particulate OP and water-soluble organic carbon (Szigeti et al., 2015; Verma et al., 2012). The link between the OP metrics and EC might be caused by some redox active compounds (i.e., quinones) adsorbed at the surface of the EC rather than by EC itself. There is no simple explanation for the associations observed between some major soluble ions and OP metrics.

4.4. Spatial variability in an office building: How to perform representative indoor PM sampling?

The lack of any major indoor PM sources and by applying similar air exchange rates, it is expected that the $PM_{2.5}$ mass concentration values are similar in all offices in a modern building if the same mechanical ventilation system is used to supply fresh air into the offices. In the case of the Dutch office building (NL3), we obtained quite similar $PM_{2.5}$ mass concentration values for the two different offices in which the monitoring campaigns were performed simultaneously.

However, a larger deviation was observed for the OP metrics as well as for the concentration of the minor and trace PM constituents (Table A.1). The offices selected for this study were located on the same floor, with similar room dimensions, exactly the same flooring, wall and ceiling materials and office layouts. The rooms were not occupied by office workers during the sampling campaign, the windows were kept closed and the difference in the air exchange rate values were less than 5%. Consequently, it can be stated that the distribution of the minor and trace PM constituents was not homogenous in the air of the office building. Both $PM_{2.5}$ samplers were applied a flow rate of 16.7 L min^{-1} which is comparable with the inhaled air volume of a healthy male and female doing sitting activity (approximately 9 and 6.5 L min^{-1} for males and females respectively; calculated from the tidal volume and breathing cycle) as recommended by ICRP66 (1994). These findings suggest that the office workers may be exposed to health relevant PM constituents to a different extent within the same office building even if the parameters of indoor environment are similar for the offices.

4.5. Limitations of the study

This study is the first large-scale investigation of $PM_{2.5}$ oxidative activity in office buildings across Europe; however, the low number of samples collected at each site does not allow us to make any substantial comparison among the individual buildings.

It should be noted that the long sampling time (about 100 h) could lead to a bias in the determination of the real $PM_{2.5}$ exposure of office workers. For comparison, 8-h long $PM_{2.5}$ sampling was also carried out during the working hours in the Hungarian office buildings in a selected office (different (HU1-3) or same (HU4-5) office than in this study) and at the air inlet of the HVAC system (next to the sampling device used in this study) (Szigeti et al., 2014). The deviation was less than 23% between the indoor $PM_{2.5}$ mass concentration values obtained for the 8-h daily and the 100-h $PM_{2.5}$ samples and less than 18% for the indoor/outdoor mass concentration ratio with one exception (HU5). On average, the indoor $PM_{2.5}$ mass concentration was only 6% higher in the case of the 8-h $PM_{2.5}$ samples which indicates that the long sampling time might not lead to significant underestimation regarding indoor $PM_{2.5}$ mass concentration. Furthermore, less chemical analysis could be carried out in the case of samples collected by low-

volume aerosol samplers during the 8-h day shift since the collected PM mass was considerably lower compared to this study.

We assessed particulate OP through antioxidant depletion; however, other acellular assays are available with still no consensus regarding which one would characterize better the oxidative activity of PM. The different assays are sensitive towards different PM components (Ayres et al., 2003). However, the same methodology was used for the assessment of OP of PM collected at different environments which makes the comparison across these studies easier (e.g., Szigeti et al., 2014, 2015).

The strong correlation among PM constituents (especially in the case of trace elements) may cause false associations when the link between OP metrics and PM constituents is investigated. This limitation will not help to fully understand the mechanism; however, the identification of the major PM sources responsible for antioxidant depletion might be possible by multivariate statistics.

Since many trace elements may originate from different sources, it would be an advantage to have information about the chemical form of the elements which would help in the source apportionment as well as in the understanding of the mechanism behind the particle-induced toxicity. However, current instrumental analytical techniques are not capable to perform speciation analysis for many elements at trace levels.

5. Conclusions

As people spend most of their time in indoor environments, indoor air quality receives more and more attention. In the case of office buildings equipped with HVAC system, it seems that outdoor air pollution is the major factor affecting indoor $PM_{2.5}$ mass concentration. Furthermore, several parameters such as the overall efficiency of the mechanical ventilation system as well as the frequency of the windows openings determine the actual indoor $PM_{2.5}$ levels. Results suggest that the indoor sources of $PM_{2.5}$ mass concentration might be less important in office building if special activity is not carried out in the offices. Accordingly, to set a target value for the indoor $PM_{2.5}$ mass concentration might not be a priority issue in office buildings in contrast to the reduction of the outdoor $PM_{2.5}$ mass concentration by different regulations (e.g., introduction of low emission zones). However, office buildings with larger indoor/outdoor $PM_{2.5}$ mass

549 concentration ratio values may require reconsideration of the performance of ventilation system.
550 Both OP^{AA} m^{-3} and OP^{GSH} m^{-3} were generally lower indoors than outdoors; however, several
551 offices exhibited indoor/outdoor values higher than one.
552 Some questions still remain unanswered. It is clear that traffic-related trace elements (e.g., Cu)
553 are the major determinants of particulate OP; however, results suggest that indoor air chemistry
554 may also play an important role in the OP of indoor $PM_{2.5}$. Further investigation is also needed on
555 the distribution of health relevant PM constituents in indoor air.
556

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558

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569 **References**

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Table 1. Characteristics of the office buildings.

Building ID	Completion year	Location	Outdoor source for air contamination (< 50 m)	Total number of storeys (storey number for indoor sampling)	Intake position of HVAC systems (m)	Outdoor sampling height (m)
FI1	2009	Kuopio; commercial/residential area	car parking, busy road	6 (2)	façade (25 m)	4
FI2	2003	Varkaus, industrial, residential area	car parking, railway	4 (2)	façade (10 m)	1.5
FI3	2004	Varkaus; city center, densely packed housing	car parking, busy road	3 (2)	façade (12 m)	1.5
GR1	2003	Athens; suburban, with larger gardens	car parking	2 (0)	façade (8 m)	1.5
GR2	2004	Athens; commercial area	busy road, quarry works	2 (1)	façade (25 m)	3.5
GR3	2010	Athens; commercial/residential area	busy road, railway station	7 (3)	roof (20 m)	13.5
GR4	1994	Athens; industrial area	car parking, busy road, highway	2 (0)	roof (10 m)	1.5
GR5	1996[a]	Athens; industrial area	car parking	2 (2)	roof (8 m)	3.5
HU1	2007	Budapest; commercial/residential area	busy road	8 (4)	façade (30 m)	30
HU2	2006	Budapest; commercial/residential area	car parking, busy road	16 (11)	roof (65 m)	66
HU3	1995	Budapest; city center, densely packed housing	car parking, busy road	11 (3)	roof (37 m)	38
HU4	2008	Budapest; commercial/residential area	car parking, busy road, railway	8 (3)	roof (27 m)	28
HU5	2009	Budapest; industrial/residential area	car parking, busy road	8 (3)	roof (30 m)	31
IT1	1970	Milan; commercial area	car parking	7 (2)	roof (25 m)	10
IT2	2006	Milan; commercial area	car parking, low-traffic road	5 (3)	roof (20 m)	15
IT3	2009	Florence; commercial/residential area	car parking	4 (2)	roof (22 m)	22
IT4	2009	Florence; commercial/residential area	car parking	4 (2)	roof (22 m)	15
NL1	1965	Noordwijk; rural area	car parking	4 (3)	roof (15 m)	16
NL2	1999	Delf; industrial/residential area	car parking, busy road	5 (1)	roof (20 m)	21
NL3	2003	Delf; commercial/residential area	car parking	7 (3)	roof (30 m)	31

[a] The building was converted in 2000.

Table 2. Minimum, mean and maximum mass concentration (μg m^{-3}) of indoor and outdoor $PM_{2.5}$ as well as the indoor/outdoor $PM_{2.5}$ mass concentration ratios observed for the summer and winter sampling campaigns. Median values are also indicated for the larger dataset.

	$PM_{2.5}$ mass concentration (μg m^{-3}; min - mean (median) - max)				indoor/outdoor mass concentration ratio (min – mean (median) - max)	
	summer		winter			
	indoor	outdoor	indoor	outdoor	summer	winter
FI	2.6 - 3.4 – 5.3	3.7 - 7.5 - 12.0	3.4 - 4.8 - 6.3	4.8 – 6.2 – 8.7	0.35 - 0.50 - 0.71	0.66 - 0.80 - 1.02
GR	8.7 - 13.3 - 16.8	14.5 - 25.4 - 31.2	5.5 - 14.3 - 18.5	9.5 - 20.8 - 26.0	0.45 - 0.53 - 0.60	0.57 - 0.68 - 0.86
HU	5.5 - 9.4 - 17.1	9.3 - 16.2 - 27.8	12.9 - 21.3 - 32.3	34.7 - 41.1 - 47.3	0.28 - 0.62 - 0.94	0.27 - 0.52 - 0.73
IT	8.9 - 10.5 - 12.6	9.3 - 10.1 - 11.1	6.1 - 11.0 - 17.7	8.6 - 27.8 - 62.4	0.89 - 1.05 - 1.35	0.28 - 0.58 - 0.73
NL[a]	4.2 - 5.2 - 6.1	9.4 - 10.8 - 12.2	5.0 - 8.4 - 12.8	6.1 - 23.7 - 33.6	0.42 - 0.48 - 0.58	0.24 - 0.48 - 0.81
All	*2.6 – 9.0 (8.7) - 17.1*	*3.7 - 15.4 (12.1) - 31.2*	*3.4 – 13.2 (12.9) - 32.3*	*6.1 - 25.4 (25.5) - 62.4*	*0.28 - 0.62 (0.58)- 1.35*	*0.24 - 0.61 (0.58)- 1.02*

[a] Additional samples collected in April and May 2013 are included in winter and summer results respectively.
Abbreviations: FI = Finland; GR = Greece; HU = Hungary; IT = Italy; NL = The Netherlands

Table 3. Spearman's rank correlation coefficients between particulate oxidative potential (OP^{AA} μg^{-1} and OP^{GSH} μg^{-1}) and the concentration ($\mu g\ g^{-1}$) of the investigated aerosol constituents. Significant correlations are highlighted.

	OP^{AA}			OP^{GSH}		
	indoor (n=24)	outdoor (n=22)	all sites (n=46)	indoor (n=24)	outdoor (n=22)	all sites (n=46)
Carbonaceous fractions						
OC	-0.06	0.37	0.30	0.07	0.71**	0.48**
EC	0.13	0.49*	0.30	0.05	0.52*	0.29
Major water-soluble ions						
NH_4^+	-0.15	-0.14	-0.12	-0.39	-0.46	-0.38
Na^+	0.14	-0.02	0.03	0.21	-0.22	-0.03
K^+	-0.24	0.63**	0.33*	-0.19	0.35	0.17
Ca^{2+}	-0.22	-0.20	-0.30	-0.14	-0.18	-0.25
Mg^{2+}	0.08	0.01	-0.01	0.31	0.00	0.11
SO_4^{2-}	-0.04	0.13	0.08	-0.16	-0.30	-0.12
NO_3^-	0.29	-0.20	-0.03	0.78**	-0.31	0.13
Cl^-	0.37	-0.40	-0.08	0.53**	-0.27	0.08
Aqua regia extractable part of trace elements						
Al	-0.15	0.30	0.07	0.04	0.42	0.15
V	0.07	0.42	0.23	0.17	-0.02	0.09
Cr	0.25	0.44*	0.44**	-0.02	0.23	0.13
Mn	0.01	0.28	0.05	-0.19	0.15	-0.11
Fe	-0.13	0.46*	0.11	-0.59	0.37	-0.18
Co	0.15	0.43*	0.19	0.22	0.08	0.08
Ni	0.18	0.59**	0.34*	0.19	0.29	0.26
Cu	0.48*	0.87**	0.67**	0.65**	0.48*	0.58**
Zn	0.13	0.40	0.24	-0.34	0.03	-0.16
Rb	-0.07	0.37	0.16	-0.37	0.07	-0.14
Sr	0.14	0.31	0.23	0.40	0.24	0.32*
Mo	0.44*	0.23	0.30*	0.50*	0.10	0.32*
Cd	0.16	0.49*	0.44**	-0.10	0.53*	0.33*
Sn	0.32	0.53*	0.42**	0.42*	0.76**	0.52**
Pb	0.14	0.43*	0.34*	0.05	0.22	0.19
Water-soluble part of trace elements						
Al	-0.28	0.51*	0.13	-0.29	0.47*	0.00
V	0.11	0.41	0.24	0.18	-0.03	0.09
Cr	0.25	0.44*	0.41**	-0.02	0.29	0.16

Mn	0.04	0.04	-0.10	-0.30	-0.15	-0.38
Fe	0.21	0.75**	0.39**	-0.42	0.34	-0.20
Co	0.13	0.17	0.04	0.38	-0.34	0.01
Ni	0.23	0.56**	0.35*	0.20	0.13	0.16
Cu	0.43*	0.76**	0.58*	0.59**	0.53*	0.54**
Zn	0.17	0.36	0.23	-0.37	-0.02	-0.20
Rb	0.05	0.29	0.19	-0.44	-0.01	-0.23
Sr	0.07	0.20	0.12	0.23	0.12	0.13
Mo	0.39	0.26	0.33*	0.35	0.15	0.27
Cd	0.01	0.53*	0.38**	-0.37	0.38	0.09
Sn	0.10	0.41	0.41**	0.03	0.19	0.22
Sb	0.39	0.61**	0.55**	0.03	0.38	0.23
Pb	0.14	0.35	0.32*	0.01	0.01	0.07

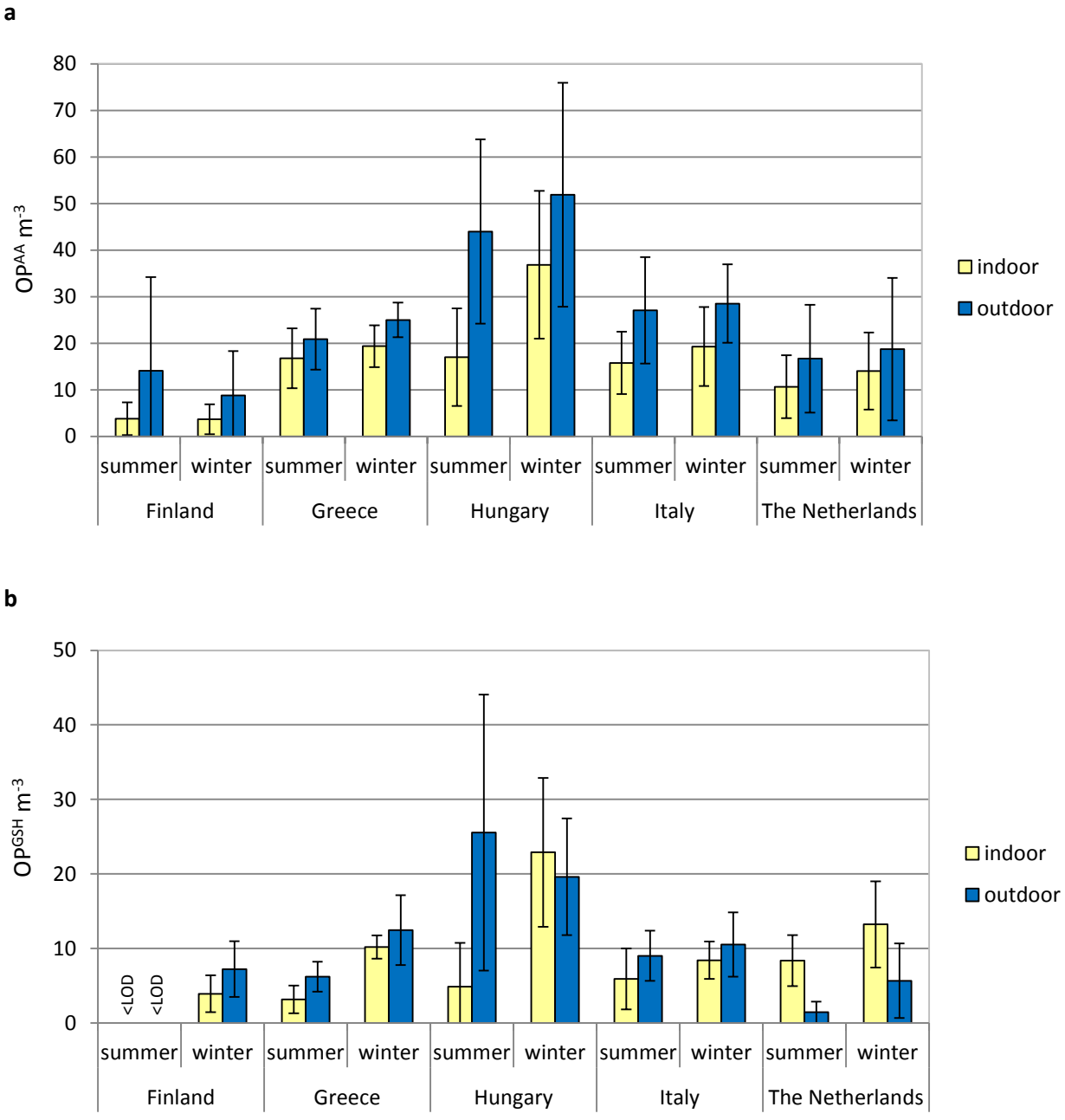
* $p<0.05$ level
** $p<0.01$ level

Figure Captions

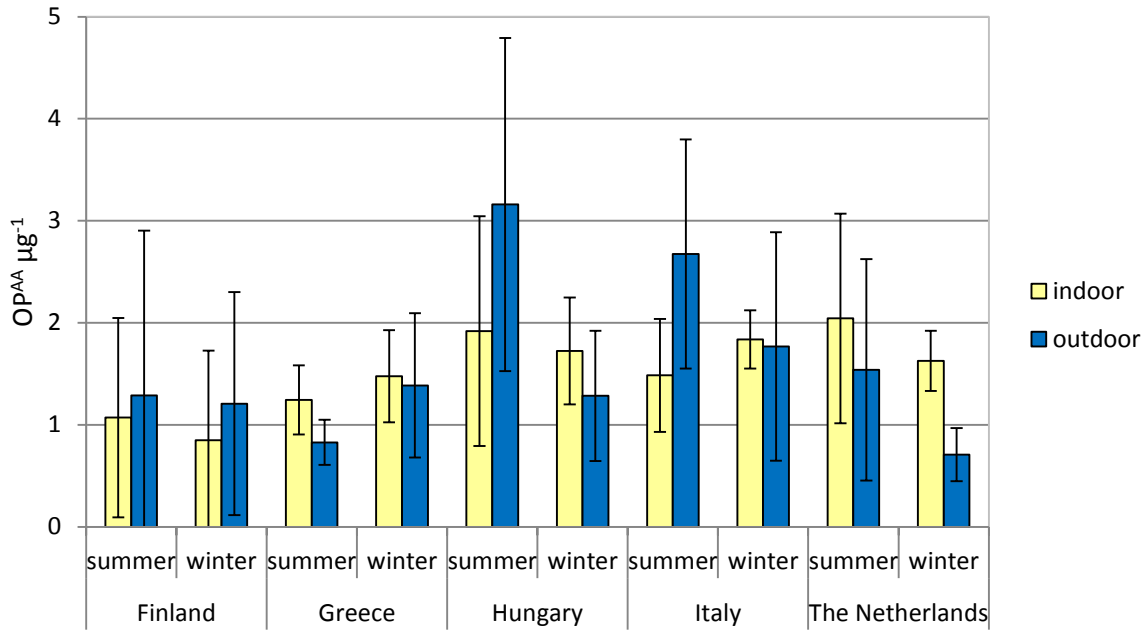
Figure 1. Seasonal and spatial variation of ascorbate and glutathione oxidative potential per unit volume (OP^{AA} m^{-3} /a/ and OP^{GSH} m^{-3} /b/;% depletion/m^3 air; mean ± standard deviation) and per unit mass (OP^{AA} μg^{-1} /c/ and OP^{GSH} μg^{-1} /d/;% depletion/μg PM; mean ± standard deviation) for the indoor and outdoor $PM_{2.5}$.
Abbreviation: LOD = limit of detection

Figure 2. Contribution (expressed in %) of the PM constituents to the indoor and outdoor $PM_{2.5}$ mass during summer (a) and winter (b). The outdoor mean temperature values are also indicated.
*Samples were collected in spring (April and May); however, they are depicted among the other results obtained for the samples collected in summer (May) and winter (April).
Abbreviations: OM = organic matter; EC = elemental carbon; nss-sulfate = non-sea-salt sulfate

Figure 1


a
80
70
60
50
40
30
20
10
0
OPAA m-3
summer
winter
Finland
Greece
Hungary
Italy
The Netherlands
indoor
outdoor
b
50
40
30
20
10
0
OPGSH m-3
<LOD
<LOD
summer
winter
Finland
Greece
Hungary
Italy
The Netherlands
indoor
outdoor

c


5
4
3
2
1
0
OP^AA µg^-1
indoor
outdoor
summer
winter
Finland
Greece
Hungary
Italy
The Netherlands

d

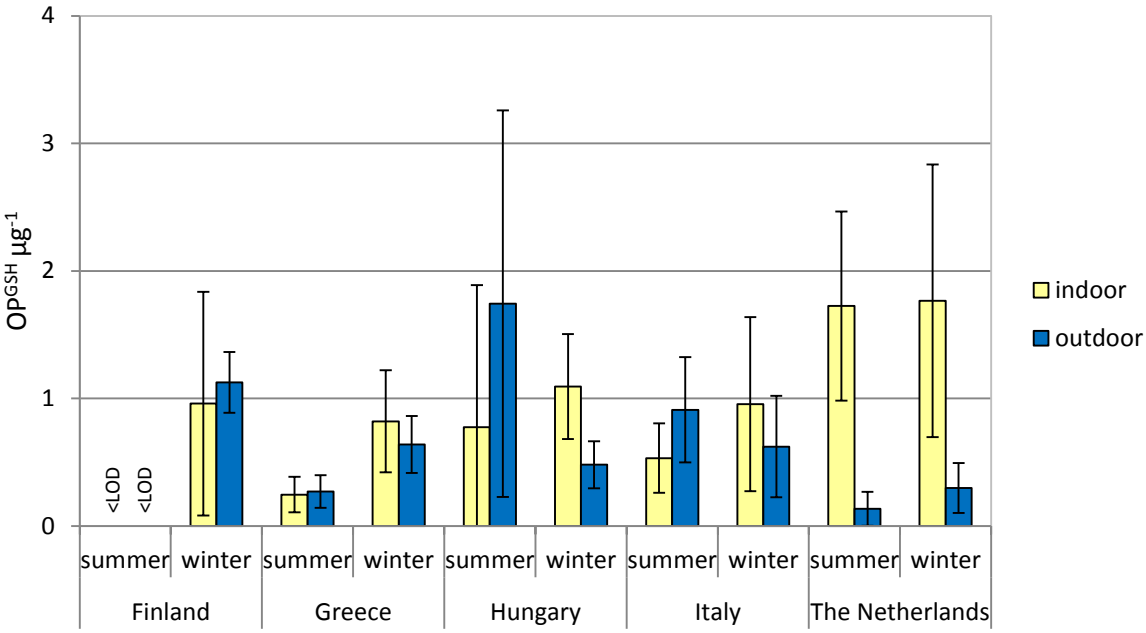
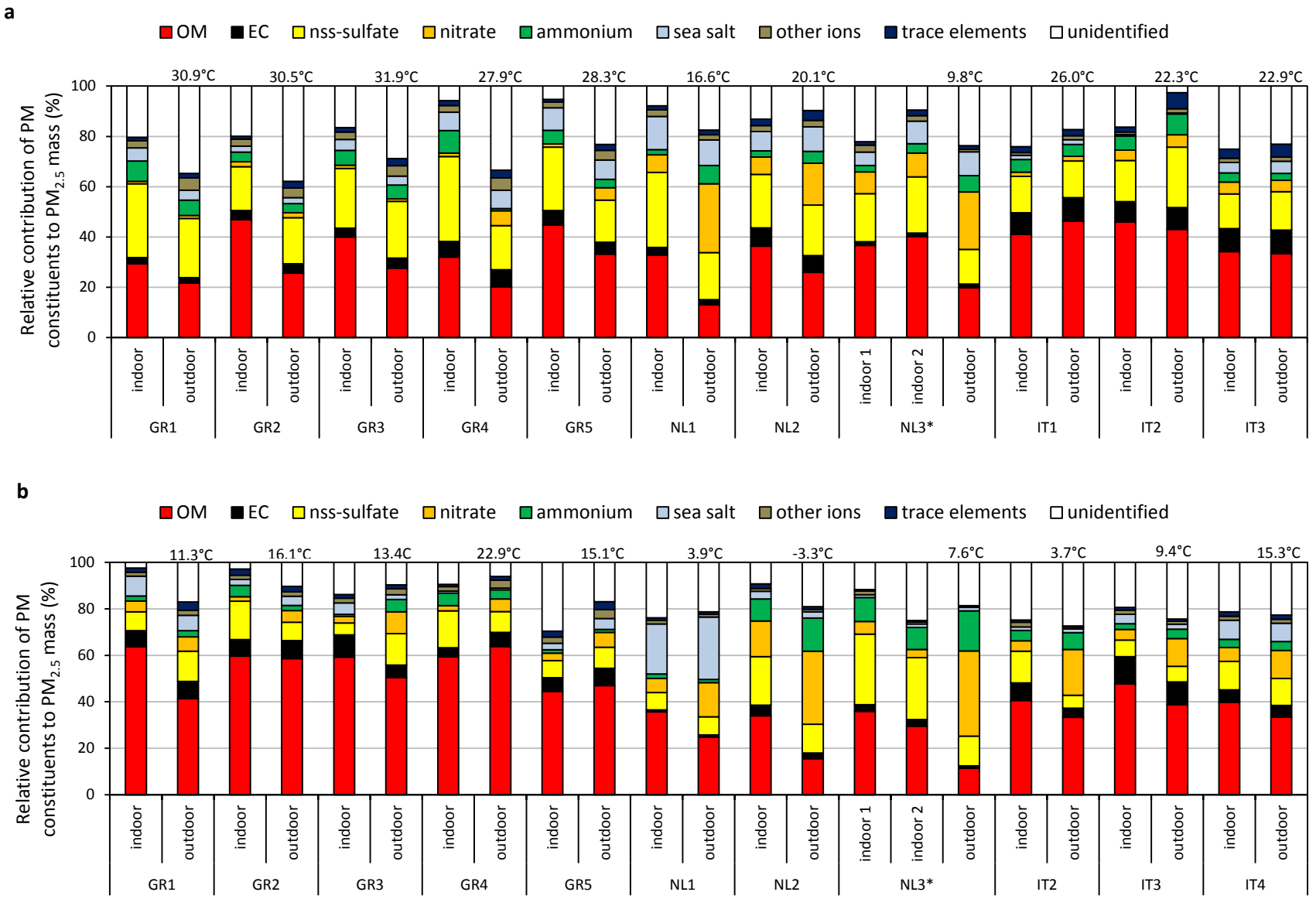

4
3
2
1
0
OP^GSH µg^-1
<LOD
<LOD
indoor
outdoor
summer
winter
Finland
Greece
Hungary
Italy
The Netherlands

Figure 2


a
OM
EC
nss-sulfate
nitrate
ammonium
sea salt
other ions
trace elements
unidentified
Relative contribution of PM constituents to PM2.5 mass (%)
30.9°C
30.5°C
31.9°C
27.9°C
28.3°C
16.6°C
20.1°C
9.8°C
26.0°C
22.3°C
22.9°C
indoor
outdoor
indoor 1
indoor 2
GR1
GR2
GR3
GR4
GR5
NL1
NL2
NL3*
IT1
IT2
IT3
b
11.3°C
16.1°C
13.4C
22.9°C
15.1°C
3.9°C
-3.3°C
7.6°C
3.7°C
9.4°C
15.3°C
IT4

Highlights

- $PM_{2.5}$ mass concentration and oxidative potential (OP) varied markedly across Europe.
- The I/O $PM_{2.5}$ mass concentration ratio was less than one with two exceptions.
- Generally, it is better to stay indoors than outdoors regarding particulate OP.
- OP metrics were associated mainly with traffic-related trace elements (e.g., Cu).
- Indoor air chemistry may play an important role in the OP of indoor PM.

SUPPORTING INFORMATION

Oxidative potential and chemical composition of $PM_{2.5}$ in office buildings across Europe – The OFFICAIR study

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Table A.1. Concentration of $PM_{2.5}$ mass and the investigated constituents as well as the oxidative potential (OP^{AA} m^{-3}, OP^{GSH} m^{-3}) for the indoor and outdoor samples collected at NL3. The deviation between the results obtained for the two parallel indoor samples are also listed.

	winter campaign			summer campaign			deviation between indoor 1 and 2 (%;[a])	
	indoor 1	indoor 2	outdoor	indoor 1	indoor 2	outdoor	winter campaign	summer campaign
mass concentration (μg m^{-3})								
$PM_{2.5}$	6.82	8.24	31.4	4.24	4.10	9.44	21	-3
oxidative potential (per m^3)								
OP^{AA}	9.43 ± 1.05	14.2 ± 1.5	19.5 ± 3.0	3.18 ± 1.41	6.90 ± 0.74	6.84 ± 0.99	51	117
OP^{GSH}	5.78 ± 2.89	11.7 ± 1.2	2.67 ± 0.71	4.13 ± 1.37	9.81 ± 0.35	0.71 ± 0.92	102	138
OP^{TOT}	15.2 ± 3.9	25.9 ± 2.7	22.2 ± 3.7	7.31 ± 2.78	16.7 ± 1.1	7.55 ± 1.91	70	128
carbonaceous compounds (μg m^{-3})								
OC	1.53	1.52	2.23	0.97	1.03	1.17	-1	6
EC	0.19	0.23	0.34	0.06	0.06	0.13	18	-5
major water-soluble ions (μg m^{-3})								
NH_4^+	0.71	0.78	5.43	0.11	0.15	0.61	11	42
Na^+	0.04	0.06	0.12	0.15	0.23	0.43	28	54
K^+	0.08	0.06	0.09	0.07	0.04	0.04	-21	-50
Ca^{2+}	0.03	0.01	0.05	0.06	0.07	0.09	-65	27
Mg^{2+}	0.01	0.01	0.03	0.03	0.03	0.05	-19	7
SO_4^{2-}	2.09	2.21	4.03	0.84	0.98	1.41	6	16
NO_3^-	0.36	0.29	11.5	0.37	0.39	2.16	-20	4
Cl^-	0.02	0.04	0.31	0.01	0.03	0.27	94	379
aqua regia extractable part of trace elements (ng m^{-3})								
Al	<13.9	<13.9	<46.4	<46.4	58.1	88.6	n.a.	>25
V	1.00	1.43	2.07	0.74	1.10	1.55	43	49
Cr	<0.75	<0.75	<0.75	<0.75	<2.51	<0.75	n.a.	n.a.
Mn	1.02	1.26	2.19	<0.80	0.86	1.18	24	>8
Fe	<23.3	26.6	55.2	<23.3	<23.3	30.0	>14	n.a.
Co	<0.049	0.050	0.076	<0.049	<0.049	0.055	>2	n.a.
Ni	<1.88	<1.88	2.12	<1.88	<1.88	<1.88	n.a.	n.a.
Cu	4.47	5.92	4.58	1.79	8.31	<1.56	32	364
Zn	<11.4	<11.4	19.9	<11.4	<11.4	<11.4	n.a.	n.a.
Rb	<0.16	<0.53	<0.53	<0.16	<0.16	<0.16	n.a.	n.a.
Sr	<0.33	<0.33	<0.33	<1.09	<1.09	<1.09	n.a.	n.a.
Mo	<0.42	0.45	0.69	<0.42	<0.42	<0.42	>7	n.a.
Cd	<0.11	0.12	0.17	<0.11	<0.11	<0.11	>9	n.a.
Sn	<1.35	1.39	1.69	<0.40	<1.35	<0.40	>3	n.a.
Sb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Pb	3.70	2.99	4.14	<1.10	1.31	1.63	-19	>19
water-soluble part of trace elements (ng m^{-3})								

Al	<0.51	<1.72	<1.72	<1.72	<1.72	1.91	n.a.	n.a.
V	0.90	1.15	1.84	0.75	0.90	1.21	28	20
Cr	<0.21	<0.21	<0.72	<0.72	<0.72	<0.21	n.a.	n.a.
Mn	<0.38	0.39	1.58	<0.38	<0.38	0.53	>3	n.a.
Fe	1.47	2.50	12.6	1.77	1.56	4.15	70	-12
Co	0.019	0.021	0.058	0.019	0.018	0.035	13	-4
Ni	0.53	0.63	1.29	0.54	0.64	0.65	19	18
Cu	1.86	3.71	2.12	1.61	6.07	0.94	99	277
Zn	5.50	7.18	18.8	1.27	2.50	3.96	31	96
Rb	0.09	0.11	0.19	0.041	0.044	0.065	26	8
Sr	0.08	0.08	0.22	0.19	0.35	0.23	4	83
Mo	<0.34	<0.34	0.61	<0.34	<0.34	<0.34	n.a.	n.a.
Cd	<0.11	<0.11	0.12	<0.032	<0.11	<0.11	n.a.	n.a.
Sn	<0.18	<0.18	0.19	<0.18	<0.18	<0.18	n.a.	n.a.
Sb	0.31	0.39	0.66	0.23	0.25	0.32	23	12
Pb	0.13	0.13	0.76	0.19	0.18	0.28	2	-6

n.a. = not applicable

[a] indoor 2 is related to indoor 1

Fig. A.1. Location of the sampling sites in Europe. The number of the investigated office buildings is also indicated on the map.

Fig. A.2. Scatter plot for the sum of the molar concentrations of the water-soluble cations multiplied with their corresponding charge and the sum calculated for the water-soluble anions.

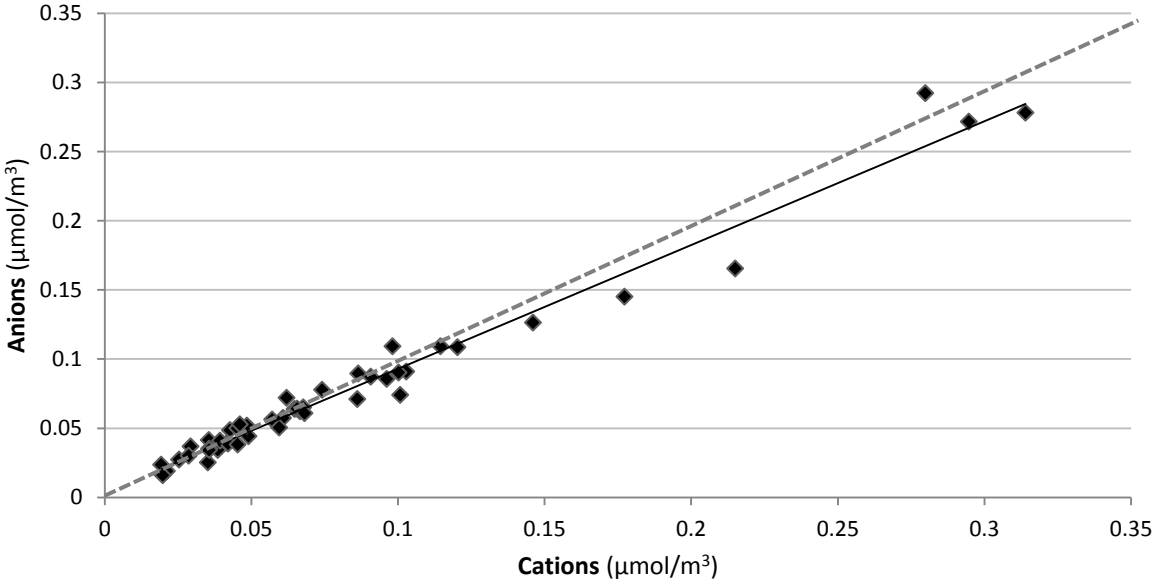

Fig. A.3. Ratios of indoor and outdoor trace element concentration values obtained for *aqua regia* extractions. Concentration is expressed in ng m^{-3} (a) and µg g^{-1} (b). Inner squares in each box correspond to the mean value. The bottom, middle and top of each box correspond to the 25th, 50th and 75th percentile while whiskers indicate 10th and 90th percentiles. Individual outliers are also shown. Data lower than LOD was rejected from the calculation.

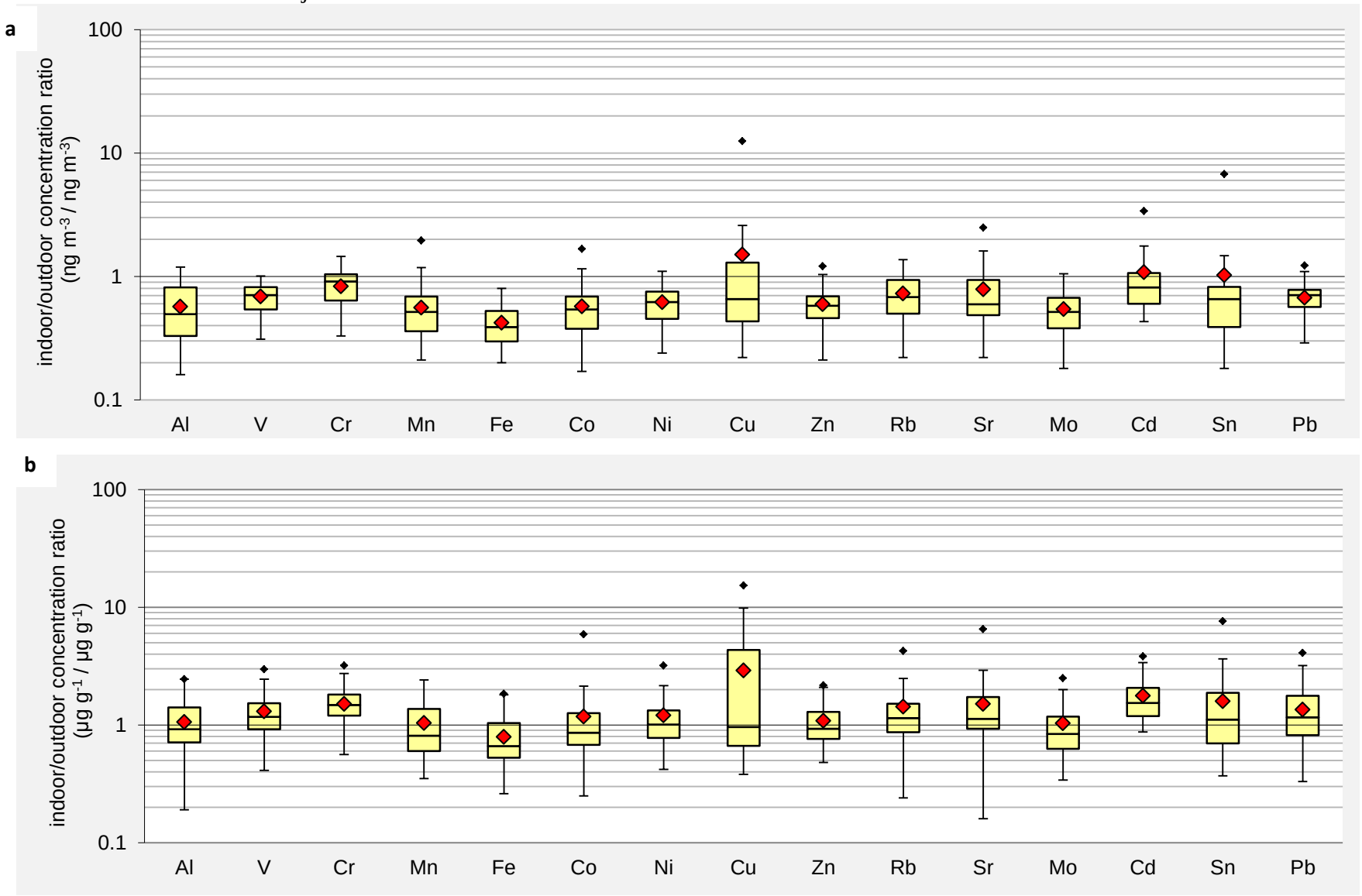

Fig. A.4. Ratios of trace element concentrations obtained for water and *aqua regia* extractions for the $PM_{2.5}$ samples collected in Greece (a), The Netherlands (b) and Italy (c). Inner squares in each box correspond to the mean value. The bottom, middle and top of each box correspond to the 25th, 50th and 75th percentile while whiskers indicate 10th and 90th percentiles. Individual outliers are also shown. Data lower than LOD was rejected from the calculation.